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DEVELOPMENT OF HYDROCARBON ANALYSES

AS A MEANS OF DETECTING LIFE IN SPACE

Contract No. NASw-508

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Principal Investigator:

W. G. Meinschein

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SUMMARY

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Irradiation of solid methane with γ -rays yields liquid alkanes which have lower mean molecular weights, less structural order, and smaller n-paraffin contents than biological or sedimental alkanes. Bacteria and kelp contain hydrocarbons that are chromatographically equivalent to 2,6,10-trimethylpentadecane, pristane, phytane, and 2,6,10,14-tetramethylheptadecane. Benzene extracts of a 2.5 billion year old Soudan sediment are rich in free sulfur and alkanes. Distributions of alkanes in the wash and extracts of the Soudan rock indicate an indigenous origin and a natural fractionation of these compounds. Pristane and phytane are apparently present in high concentrations in the hydrocarbons from the Soudan chert and Murray meteorite. n-Paraffins in the Murray and Orgueil carbonaceous chondrites are differently distributed. The Murray n-paraffins do not show an "odd carbon preference" as do the n-paraffins from the Orgueil meteorite. Similar distributional differences are observed in alkanes from some ancient and recent sediments or biological samples on earth.

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INTRODUCTION

Carbon compounds in terrestrial sediments and biological tissues have been extensively studied. Analyses show that only a few types of compounds are found commonly in both living things and sediments. Alkanes are the most stable constituents of organisms and the most abundant biological type molecules in sedimentary environments. Many organic geochemists agree that either alkanes or fats and waxes from plant and animal remains are a major source of terrestrial hydrocarbons.

Since alkanes are stable, ubiquitous, and large molecules which may be useful in paleo- and exobiological investigations,¹ research under contract number NASw508 is evaluating whether or not C_{15} to C_{30} alkanes are reliable biological indicators. C_{15} to C_{30} alkanes were selected in preference to smaller or larger alkanes because alkanes in the 15 to 30 carbon number range are large enough to display great structural order and small enough to be definitively analyzed with available instruments.¹⁻³ Subsequent statements about alkanes in this report will refer to C_{15} to C_{30} hydrocarbons unless otherwise specified.

Previous investigations of the origins and compositions of biological and sedimental alkanes have shown that:

1. Living things contain alkanes;
2. Concentrations of alkanes in elimination products of organisms are two orders of magnitude greater than the concentrations of alkanes in biological tissues;⁴
3. Alkane concentrations in fecal and sedimental lipids are equivalent.⁴
4. Organisms have apparently made many times more alkanes than are now preserved in sediments.^{4,5,6}
5. Alkanes in some Recent sediments have C^{14} ages that indicate the time of depositions of these sediments.⁷

6. n-Paraffins and cycloalkanes in Recent and some ancient sediments and living things have carbon number distributional patterns that are similar and presently unique to these samples.^{8,9}
7. Pristane (2,6,10,14-tetramethylpentadecane) has been identified in living things and in alkanes from sediments of many geological ages.^{4,10-17}
8. Phytane (2,6,10,14-tetramethylhexadecane), farnesane (2,6,10-trimethyldodecane), nor-farnesane (2,6,10-trimethylundecane), and 2,6,10-trimethylpentadecane have been found in appreciable concentrations in crude oils.^{13,14,16-19} All of these compounds have carbon skeletons identical to those found in known biological alcohols.
9. Tetra- and pentacyclic alkanes in most living things, Recent and ancient sediments have similar carbon number distributions and mass spectral cracking patterns.^{4,8,9}
10. Optical activities of alkanes in biological lipids, Recent sediments, and crude oils of various geologic ages are comparable.^{4,7,17,20,21}

In essence the preceding findings have established that living things are the major source of the alkanes that are presently being incorporated in terrestrial sediments, and if previous life resembled existing life in metabolic processes and abundance, previous organisms have made many times the quantities of alkanes that are now in the sediments on earth. Correlations in the structures, distributions, optical activities, and isotopic compositions of compounds in plant and animal lipids and in alkanes from sediments of many geologic ages indicate that former organisms were metabolically similar to existing organisms and that former life was a probably source of most sedimental alkanes.

An analogy may be drawn between the manner in which fossils have been developed and alkanes are being developed as indicators of former life. Observations of living things and the changes that transform their remains provide a basis for hypotheses about what may have happened to remnants of ancient life. From these observations, it is apparent that only certain stable structures of living things may be preserved after their demise. Fossils have gained general acceptance as biological remnants because extensive morphological investigations have related fossil structures to structural features in organisms. These relationships have been traced from plants and animals to fossils from sediments of successively older geologic ages. Fossils reveal a record of the continuity of living forms on earth and of the evolution of some kinds of living things. Fossil records, also, confirm the likelihood that former life was a principal source of sedimental alkanes, and this investigation is tracing alkanes as fossils have been traced from living things back through sediments of increasing geologic ages.

Admittedly, problems associated with the development of alkanes and fossils as biological indicators are not entirely identical. Neither are the uses that may be made of fossils and alkanes equivalent. Chemical alterations can increase the stability of fossils, but extensive transformations would destroy the resemblance between a molecular remnant of life and a biological compound. Most fossils are partially mineralized. Minerals have rendered many fossils stable, but these minerals have also removed the possibility of determining the structure of the organic material they replaced. Stable biological molecules may retain the only direct evidence of the biochemistry of ancient organisms, and if these molecules are preserved, many of them can be

precisely analyzed or characterized. Finding cited above, indicate that some alkanes made in or from biological lipids do retain their structures in sediments. Analyses of alkanes may be more objectively determined than the morphologies of fossils. Analytical methods may afford additional advantages over visual methods in space probes. Analyses can be digitized and transmitted with fewer bits of information than a picture.

Data that follow will present analyses of abiotic, biological, sedimental, and meteoritic alkanes. These data will extend the findings reported above.

DISCUSSION

Some authors favor an abiotic origin of meteoritic alkanes.²²⁻²⁵ They presume an equivalence of abiotic and biotic alkanes because syntheses under primordial conditions have made many of the monomers from which biological molecules are constructed.^{26,27} This presumption has not been experimentally demonstrated, and it cannot be disproved. Abiotic reactions and products are infinitely variable. Nonetheless, an effort is being made to analyze abiotic fractions that even grossly resemble biological or sedimental alkanes. Such fractions are apparently rare. Many hydrocarbon polymers are commercially produced. These compounds and most Fischer-Tropsch products bear little resemblance to naturally occurring alkanes, but some synthetic hydrocarbons contain compounds that fall in the molecular weight range of biological alkanes. Analyses of a special Fischer-Tropsch prime oil, for example, were presented in an earlier NASw508 report.²⁸ This atypical oil contained alkanes with mean molecular weights equivalent to crude oil alkanes, but these Fischer-Tropsch alkanes are not similar to biological or sedimental alkanes.²⁸

A GLC analyses of alkanes made by the γ -ray irradiation of solid methane is shown in Figure 1. These alkanes were supplied by Dr. W. F. Libby, and it is reasonable to expect that irradiations of methane could produce liquid alkanes in primordial environments.²⁹ Data in Figure 1 show the mean carbon number of the γ -ray alkanes is 12 or less. They contain only minor concentration of $> C_{17}$ compounds, and the chromatogram does not contain sharp peaks. These alkanes differ markedly from biological alkanes as may be deduced by comparing Figures 1 and 2.

Dr. T. S. Oakwood and Dr. R. G. Stone supplied the alkanes from bacterial wax. Drs. Oakwood and Stone took precautions to prevent contamination during the isolation of these alkanes from *Vibrio ponticus*. They believe that a Sharples centrifuge was the only possible source of extraneous alkanes in the bacterial lipids,³⁰ and the GLC analyses in Figure 2 do not suggest that a lubricants from a centrifuge were added to these lipids. The latter chromatogram shows that the bacterial alkanes contain higher concentrations of C_{18} to C_{30} n-paraffins than do crude oils;⁴ whereas lubricating oils are a distillate of mainly C_{15} to C_{20} alkanes. Noteworthy, in Figure 2 are the large n- C_{15} peaks and the peaks immediately to the left of the C_{16} to C_{20} n-paraffin peaks. The latter peaks have retention temperatures and relative abundances or peak heights equivalent to isoprenoids in crude oils. With exceptions of the large n- C_{15} peak and an increase in concentrations of n-paraffins with increasing carbon number in the C_{18} or C_{19} to C_{25} range, the chromatogram of the bacterial alkanes are similar to the chromatograms of a Cretaceous crude oil.⁴

GLC analyses shown in Figures 3, 4, and 5 are of alkanes from the Nonesuch formation. This sample was provided by Dr. E. S. Barghoorn. Data in

Figures 3,4, and 5 are a partial confirmation of the identifications of pristane and phytane in this billion year old Nonesuch rock. These identifications are being published by two different research groups.^{16,17} Vanadyl porphyrins are also present in the Nonesuch siltstone, and the Nonesuch alkanes have higher optical activities than do alkanes in much younger crude oils.¹⁷ Geological and chemical evidence strongly indicate that the carbon compounds in the Nonesuch rock are indigeneous.^{17,31}

Investigations of the Nonesuch hydrocarbons and porphyrins are pertinent to the use of alkanes as biological indicators. Stability is an essential property of biological indicators because stable organic compound can retain their identities and become concentrated in biospheres. The optical activities, distributions, and structures of Nonesuch alkanes provide evidence of the remarkable stabilities of certain biological hydrocarbons.^{16,17,31} It may be argued that the diagenesis of carbonaceous material will render biotic and abiotic alkanes equivalent,¹² but analyses of the Nonesuch alkanes do not support this argument. Nor do the data that follow.

Dr. Preston Cloud, at appreciable personal risk, acquire samples of a 2.5 billion year old Soudan sediments from the abandoned Soudan Mine. GLC analyses in Figures 6,7, and 8 are of alkanes isolated from a rock and carbonaceous lens from these sediments. Dr. Cloud obtained the samples at the 21st level of the Mine approximately 1800 feet below the NW corner of the NW corner of the SW corner of section 27(62N-15W). The samples are from the lower part of Soudan Iron Formation, and they were carefully collected to prevent any chance of contamination.³¹

Analyses of the Soudan rocks also provided a check on whether or not the samples were contaminated. The rocks were extracted whole in an ultrasonicator using two separate aliquots of a solution of 1 volume methanol in 4 volumes of benzene. After this extraction; the rocks were crushed to 40 mesh in a porcelain mortar, and the crushed rock was extracted in the ultrasonicator with 3 additional aliquots of 4-1 benzene-methanol. Then, the crushed rock was treated with concentrated HF for 24 hours, and the HF treated residue was extracted as described above. Analyses of the extracts of the whole, crushed, and HF treated rocks were carried out separately. All of these extracts contained free sulfur which was removed with colloidal copper.³³ Silica gel chromatography³⁴ was used to isolate alkanes from the light yellow extracts, and GLC analyses of the three alkanes fractions are presented in Figures 6,7, and 8.

In Figure 6, a chromatogram of the alkanes in the wash, the n-paraffin peaks are largest, but the peaks immediately to the left of the n-C₁₇ and n-C₁₈ peaks, which are tentatively identified as pristane and phytane, are quite large. This extract contains n-paraffins up to n-C₂₇, and the maximum concentration of alkanes appears among compounds with retention temperatures in the n-C₁₈ to n-C₂₀ range.

The chromatogram of the alkanes from the extracts of the crushed rocks in Figure 7 differs significantly from the chromatograms in Figures 6 and 8. "Pristane" and "phytane" are the largest peaks in Figure 7, and peaks of n-paraffins containing more than 22 carbon atoms are not readily detectable in this chromatogram. These alkanes are composed predominantly of non-linear hydrocarbons, and their maximum concentration appears in compounds with retention temperatures in the range of n-C₁₈ and n-C₂₀.

Alkanes from the HF treated rock, see Figure 8, have a maximum concentration in the $n\text{-C}_{20}$ to $n\text{-C}_{22}$ range. Although the peak alkane concentrations occur at higher carbon numbers in Figure 8 than in Figure 6 and 7, the alkanes in the HF treat appear in many aspects to have a composition intermediate to those of the alkanes in the wash and crushed stone extracts. For example, the pristane and phytane concentrations are respectively lowest and highest in the latter alkane fractions.

Data in Figures 6,7, and 8 indicate that the alkanes in these fractions may have had a common origin. Alkanes released by treating the Soudan rocks with HF had probably been effectively bound in these rocks since their formation 2.4 to 2.5 billion years ago. After major rock forming processes were complete, redistribution processes most likely did not change the compositions of these bounded alkanes significantly. Thus, these alkanes may reflect the compositions of the hydrocarbons that were laid-down with the Soudan sediments more closely than do the alkanes in the wash and the extracts of the crushed stones. The latter alkanes may have been subjected to redistributions throughout the history of these rocks.^{3,9}

Chromatographic and molecular sieve processes may explain the compositional differences between the "mobile" alkanes extracted from the whole and crushed rocks. These "mobile" alkanes have similar mean molecular weights which are lower than those of the bound alkanes because lighter alkanes are more soluble, diffuse more rapidly, may be redistributed to a greater extent by ground waters than heavier alkanes, but differences between the alkanes in the wash and crushed stone extracts reflect fractionations by types rather than molecular weights. These latter differences may be partially a consequence of the structure of the Soudan rocks and the extraction procedure.

The Soudan rock is a chert containing amorphous carbon. This carbon is concentrated in lens and in stratifications within the stone. When the whole stones were extracted, they split at the carbon-rich layers exposing most of the carbon to the solvent. Alkanes in the wash probably came mainly from the carbon in the stone, and these alkanes apparently were rich in n-paraffins because n-paraffins are adsorbed more strongly on carbon than other alkanes. After the stones were finely crushed, the small pores of the chert were exposed to the solvent, and the alkanes in this fraction apparently contained those alkanes that were most mobile in these pores. Previous analyses suggest that the alkanes from the crushed rock would resemble the first fraction of the alkanes from the HF treat that could be eluted from alumina columns operated at high gel to sample ratios.³⁵ It has been proposed that such columns function as molecular sieves.³⁵ The first eluates from alumina columns contain high concentrations of branched-chain alkanes, some low molecular weight n-paraffins, and negligible amounts of large ($> C_{22}$) n-paraffins.

The preceding analyses and interpretations indicate that the fractions isolated from the Soudan rock contain some of the oldest and best fractionated alkanes that have been found in terrestrial sediments. These results and interpretations will be checked by additional analyses using other samples of the Soudan formation. However, based on available data, it is probable that pristane and phytane are indigenous to these 2.5 billion year old sediments.

Alkanes from the Murray carbonaceous chondrite, also, apparently contain pristane and phytane. GLC analysis of the Murray alkanes is shown in Figure 9. A gas chromatogram of the alkanes from the Orgueil meteorite is presented in Figure 10. The latter chromatogram has been independently confirmed

by analyses in another laboratory.³⁶ Comparisons of the chromatograms of meteoritic and terrestrial alkanes in this and previous publications^{3,4} may be of interest. The differences in the distributions of alkanes from the Murray and Orgueil chondrites appear comparable to difference observed between alkanes in the Soudan wash (Figure 6) and in kelps, see Figure 11. Both in Figures 10 and 11, the odd carbon number n-paraffin peaks are larger than the even carbon number n-paraffin peaks in the C_{23} to C_{29} range. An "odd carbon preference" in this carbon number range has only been observed in n-paraffins from the Orgueil meteorite and from some biological products^{3,4} and relatively young terrestrial sediments.^{3,4,8}

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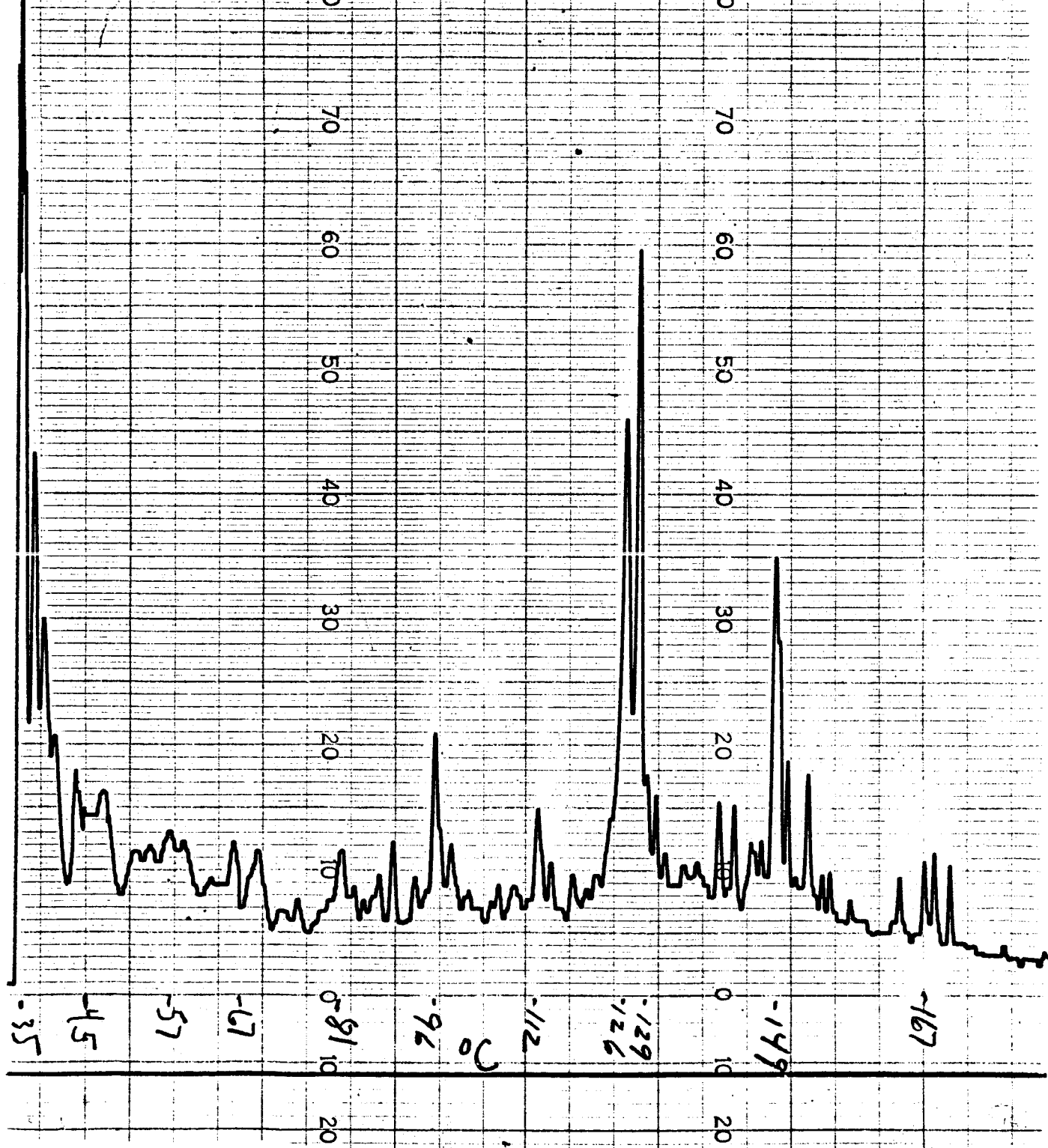
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HYDROCARBON SAMPLE (ABIOTIC) DR LIBBY

APIEZON 2" V (BARBER-COLMAN)

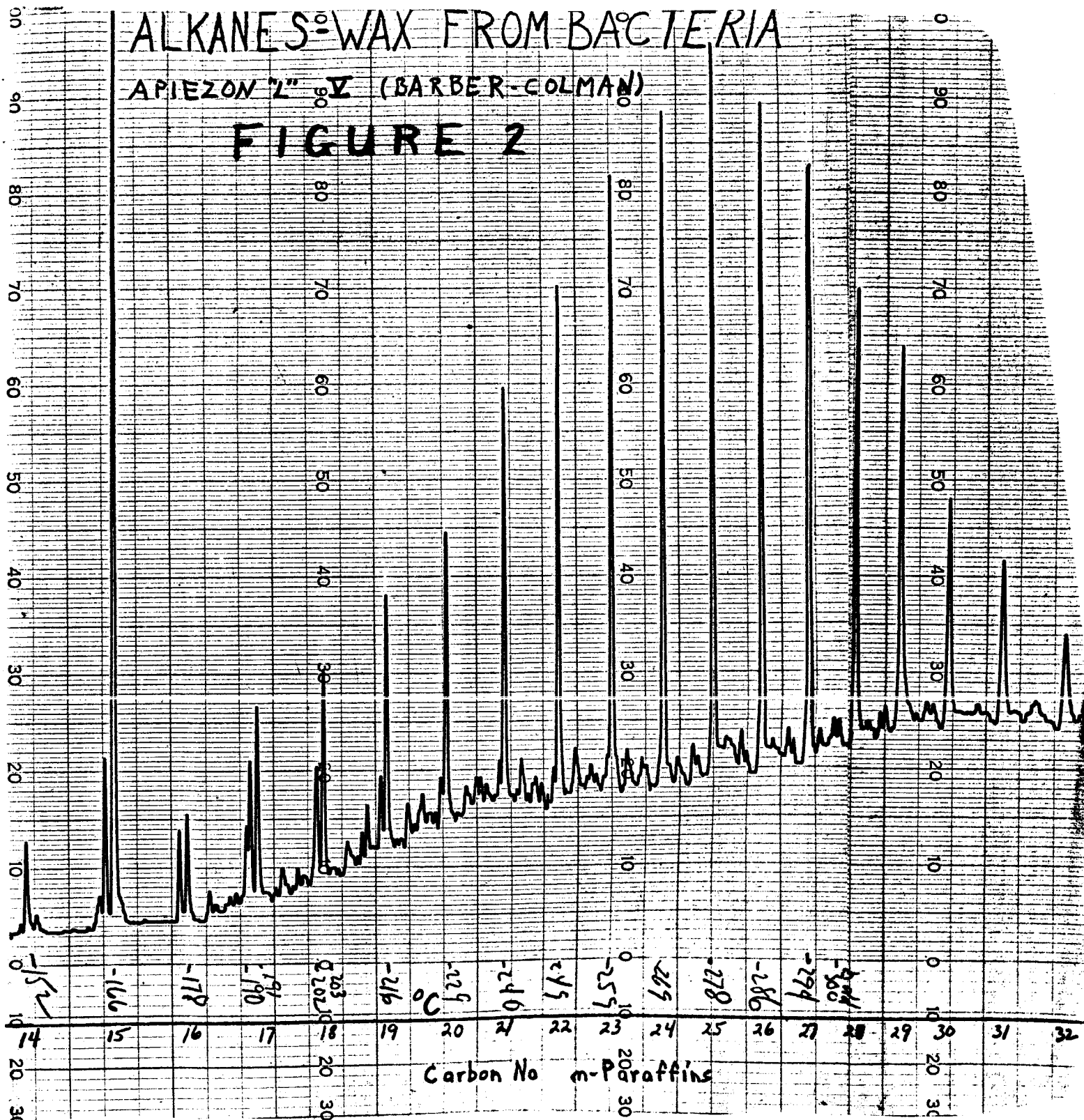
FIGURE 1



ALKANES: WAX FROM BACTERIA

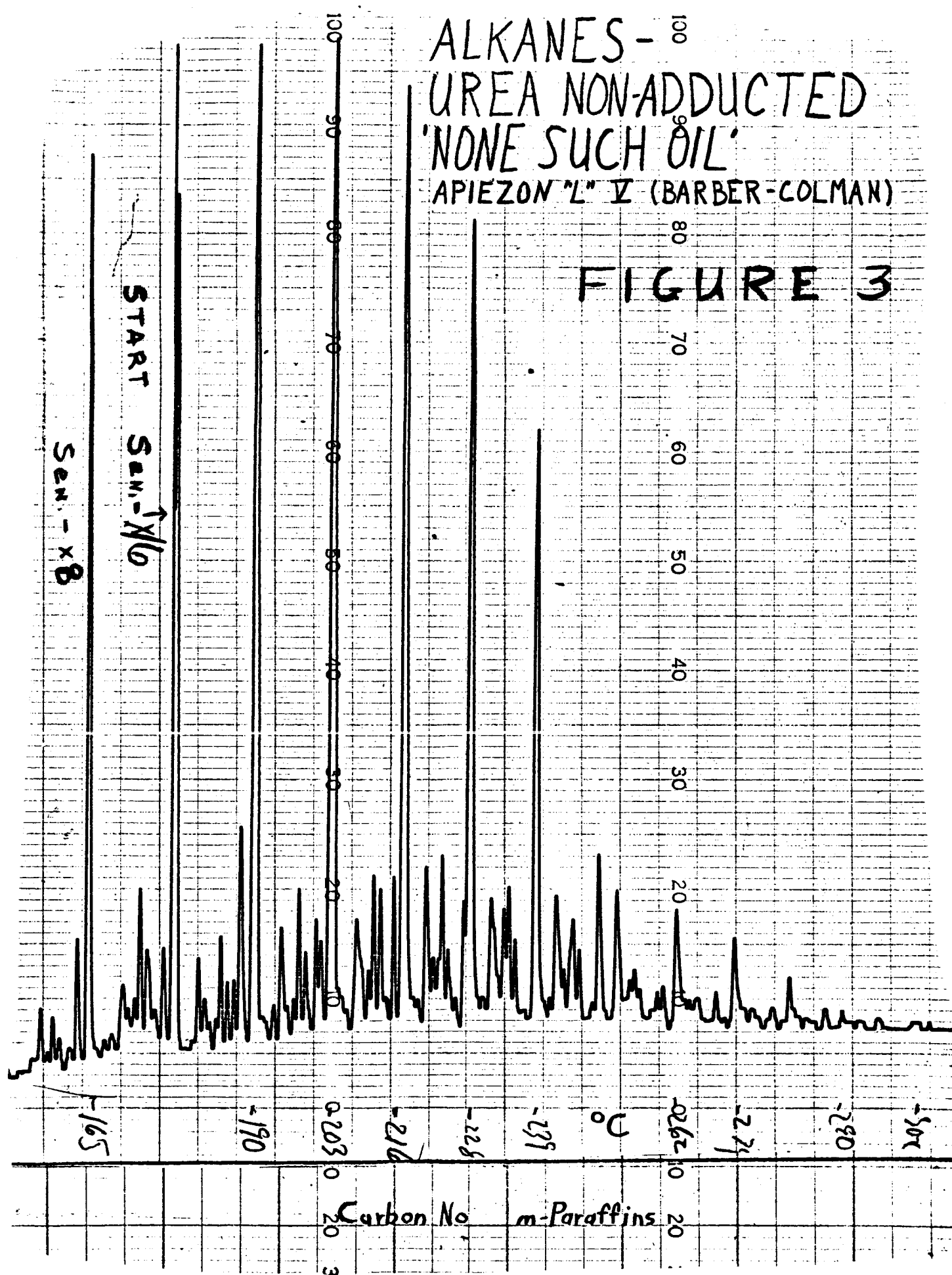
APIEZON 2" V (BARBER-COLMAN)

FIGURE 2



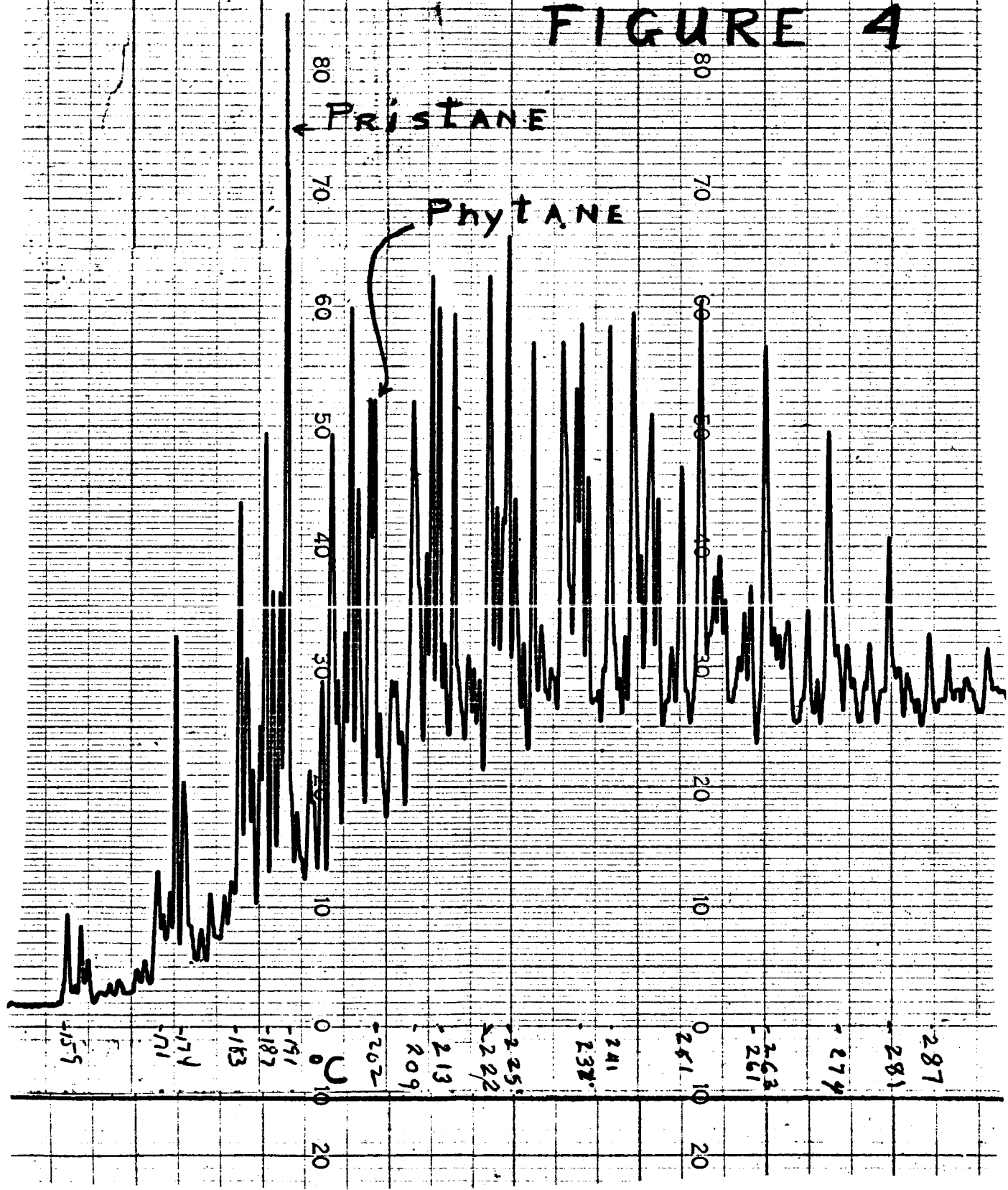
ALKANES -
 UREA NON-ADDUCTED
 'NONE SUCH OIL'
 APIEZON "L" V (BARBER-COLMAN)

FIGURE 3



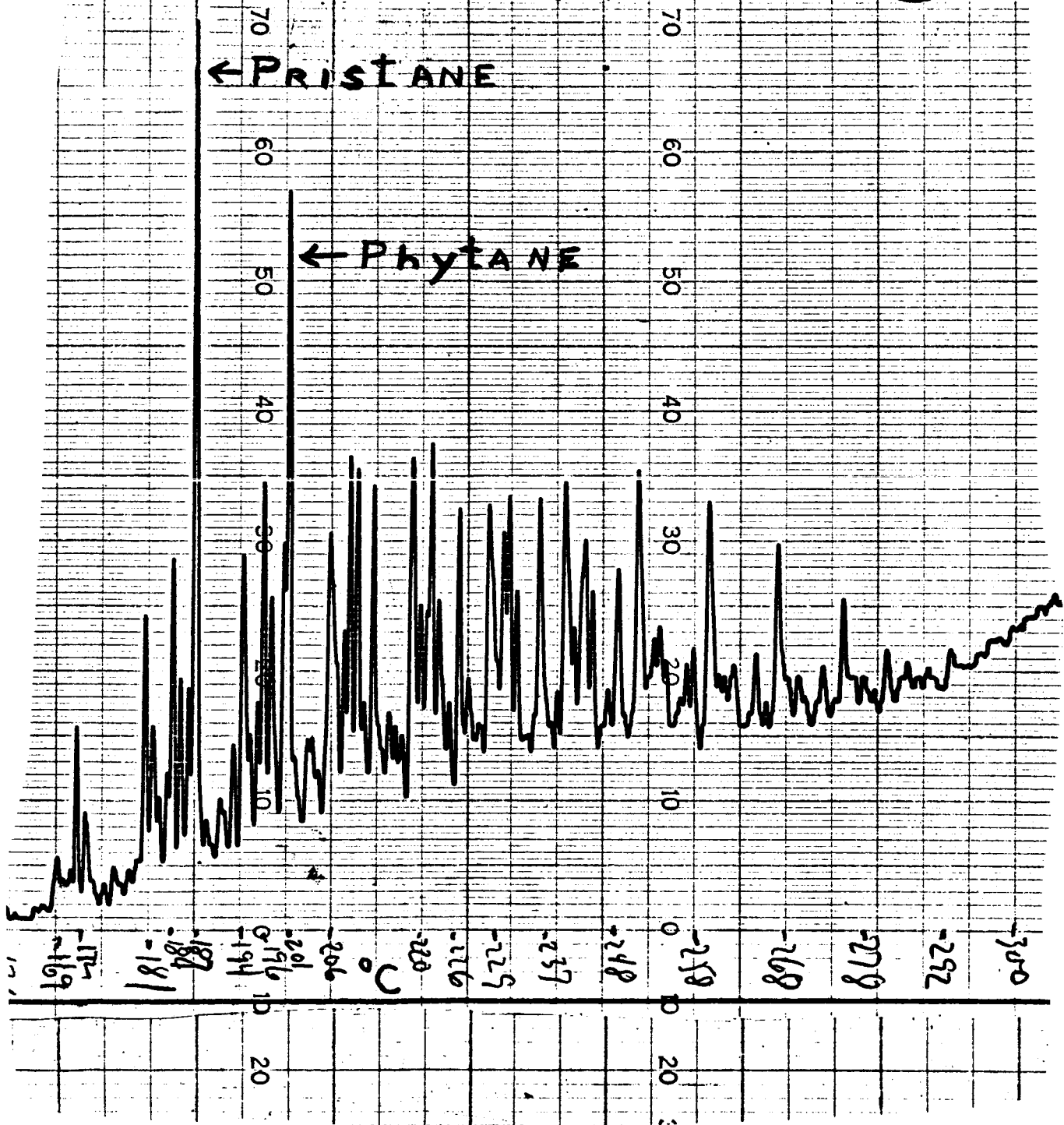
ALKANES - UREA NON-ADDUCTED
 'NONE SUCH OIL' PARAFFINS REMOVED
 APIEZON "L" V (BARBER-COLMAN)

FIGURE 4



ALKANES- UREA NON-ADDUCTED
'NONE SUCH OIL'
PARAFFINS REMOVED
PRISTANE + PHYTANE ADDED
APIEZON 'L' V (BARBER-COLMAN)

FIGURE 5



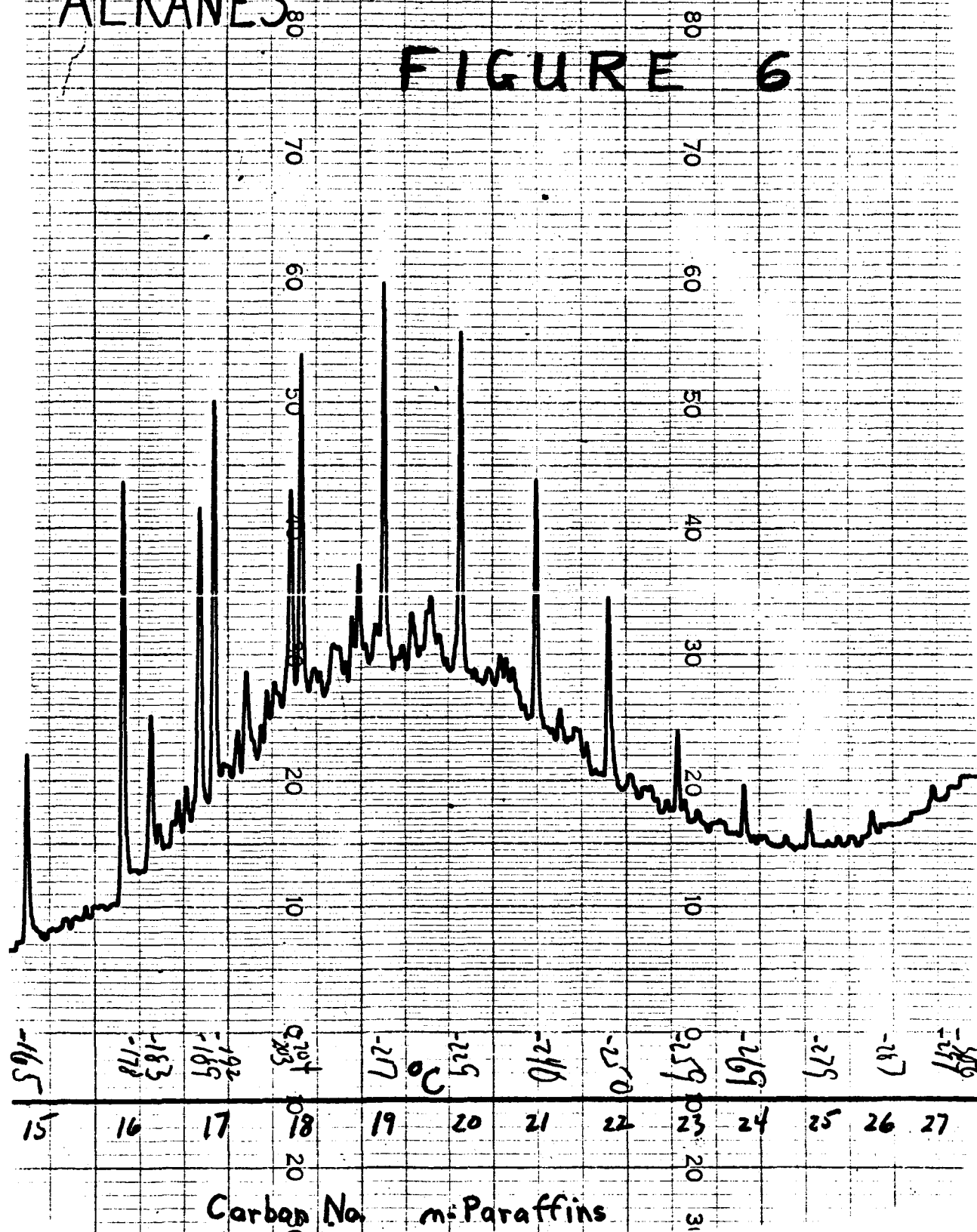
SLOUDAN MINE ROCK, SLOUDAN, MINN.

SOLVENT WASH OF ROCK

APIEZON "L" V (BARBER-COLMAN)

ALKANES

FIGURE 6



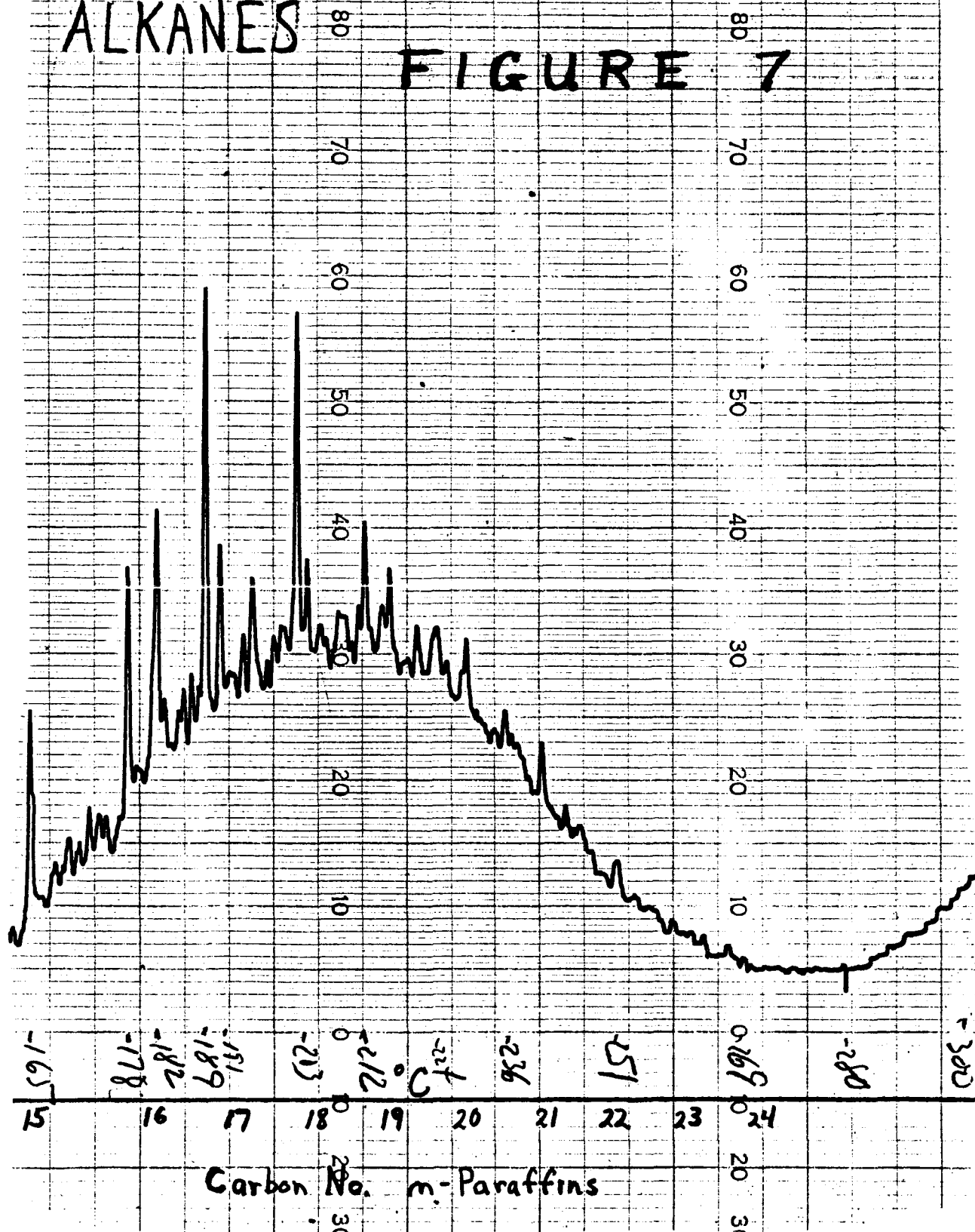
SOUDAN MINE ROCK, SOUDAN, MINN.

SOLVENT EXTRACTION OF PULVERIZED ROCK

APIEZON "L" V (BARBER-COLMAN)

ALKANES

FIGURE 7

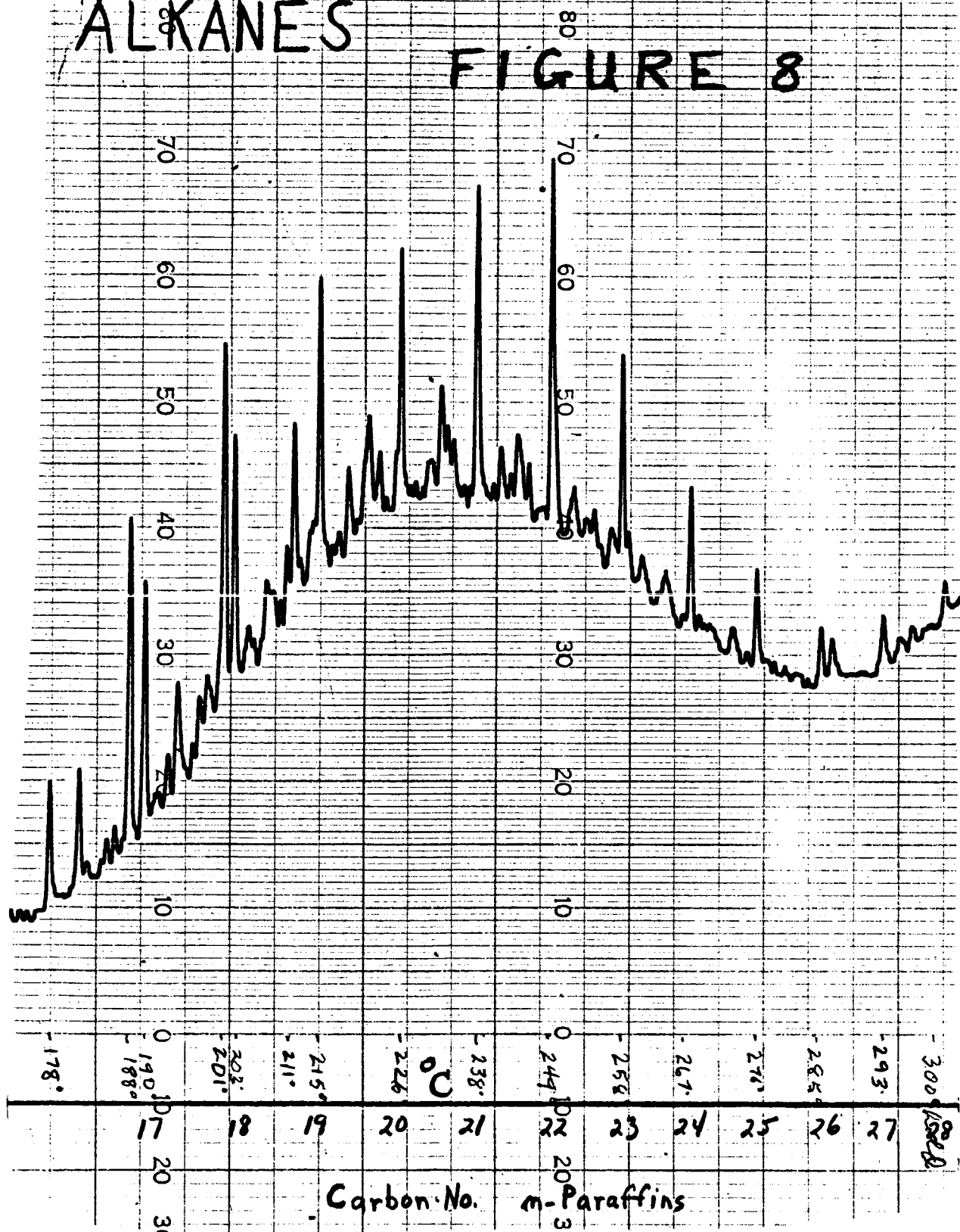


Soudan Mine Rock, Soudan, Minn.

HF EXTRACTION OF PULVERIZED ROCK
APIEZON "L" V (BARBER-COLMAN)

ALKANES

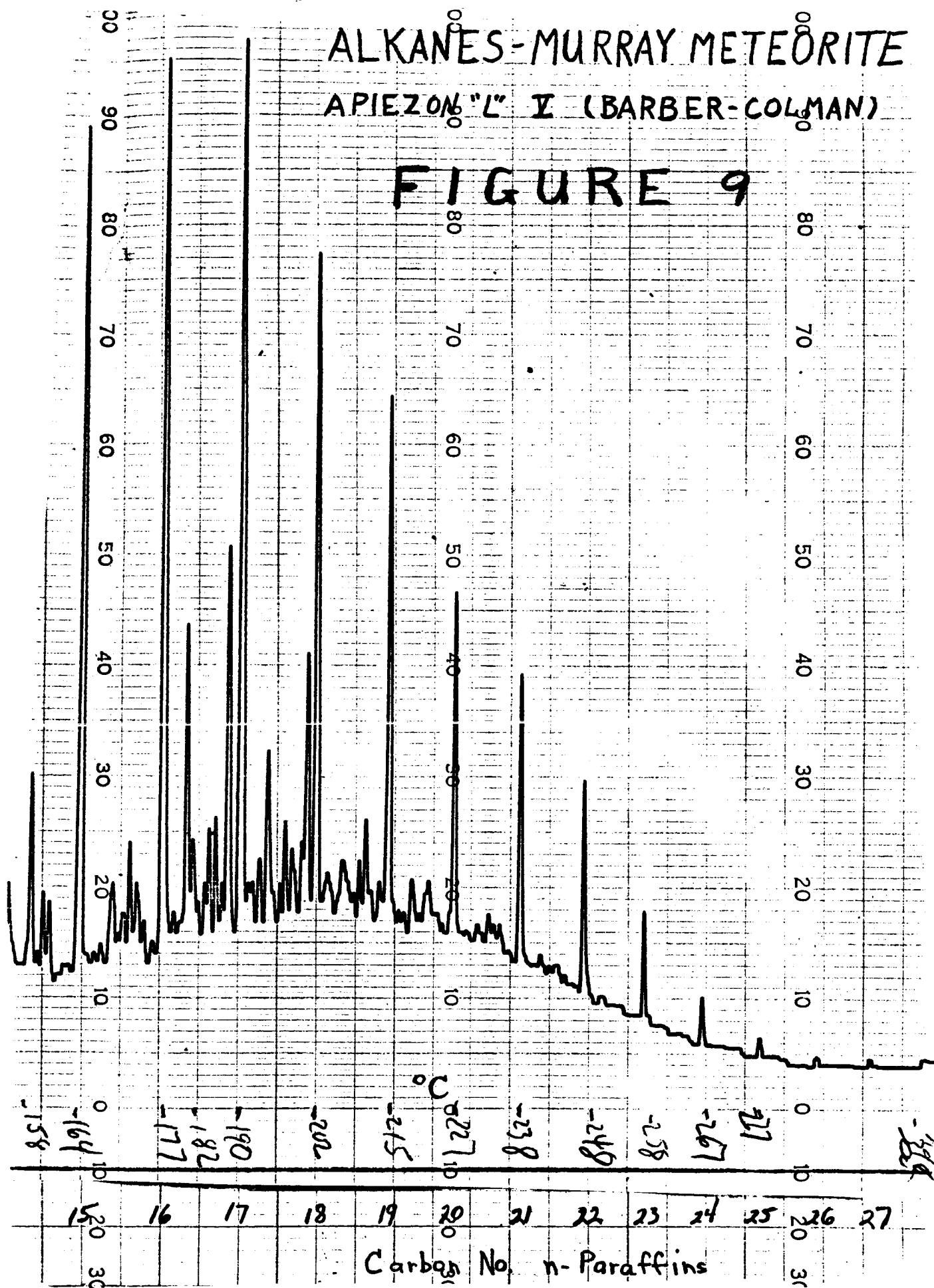
FIGURE 8



ALKANES-MURRAY METEORITE

APIEZON "L" II (BARBER-COLMAN)

FIGURE 9



ALKANES - ORGUEIL METEORITE

FIGURE 10

